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Determination of Zinc, Cadmium, Lead, and Copper in Water By Anodic Stripping Voltammetry

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The Tennessee Valley Authority developed a method of differential pulse anodic stripping voltammetry for determining total concentrations of cadmium and lead in water samples from ash ponds at steam-electric generating plants. After digestion of the sample and addition of reagents to overcome interferences by iron (III) and selenium (IV), the peak current for cadmium and lead is measured and quantified by standard addition. The effective range for this method is 0.3 to 100 µg/l of cadmium and 3 to 100 µg/l of lead. This method gives suitable accuracy for cadmium and lead in reference water samples and in split samples of effluent water from ash ponds that were analyzed by atomic absorption. Limited data show that this method probably also can be used for 5 to 100 µg/l copper but that it is unsuitable for zinc because of a 15-µg/l sample blank.

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Interagency Energy-Environment Research and Development Program Report

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DETERMINATION OF ZINC, CADMIUM, LEAD, AND COPPER IN WATER BY ANODIC STRIPPING VOLTAMMETRY

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ABSTRACT

The Tennessee Valley Authority developed a method of differential-pulse anodic stripping voltammetry for determining total concentrations of cadmium and lead in water samples from ash ponds at steam-electric generating plants. After digestion of the sample and addition of reagents to overcome interferences by iron (III) and selenium (IV), the peak current for cadmium and lead is measured and quantified by standard addition. The effective range for this method is 0.3 to 100 µg/l of cadmium and 3 to 100 µg/l of lead. This method gives suitable accuracy for cadmium and lead in reference water samples and in split samples of effluent water from ash ponds that were analyzed by atomic absorption. Limited data show that this method probably also can be used for 5 to 100 µg/l copper but that it is unsuitable for zinc because of a 15-µg/l sample blank for zinc.

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CONTENTS

	Page
Acknowledgments	iii
Abstract	iv
Figures	vi
Tables	viii
Abbreviations and Symbols	x
1. Introduction	1
2. Conclusions	4
3. Recommendations	5
4. Experimental	6
Sample Preparation	6
Equipment	7
Preparation of Equipment and Solutions	7
Determination of Cadmium and Lead by ASV	9
Determination of Copper and Zinc by ASV	11
5. Results and Discussion	12
References	17

FIGURES

Number		Page
1	Calibration curve for surface area of mercury drop formed by extrusion with a manually operated hanging mercury drop electrode	23
2	Anodic stripping voltammograms for total recoverable cadmium and lead in 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -0.800 V vs. sce into a mercury droplet with a surface area of 0.032 cm² for 2 min with stirring plus 30 s without stirring	24
3	Interference of selenium (IV) on anodic stripping voltammograms for total recoverable cadmium and lead in 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -0.800 V vs. sce into a mercury drop with a surface area of 0.032 cm² for 2 min with stirring plus 30 s without stirring	25
4	Ascorbic acid for eliminating interference of selenium (IV) on anodic stripping voltammograms for total recoverable cadmium and lead in 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -0.800 V vs. sce into a mercury droplet with a surface area of 0.032 cm² for 2 min with stirring plus 30 s without stirring	26
5	Anodic stripping voltammograms for total recoverable cadmium, lead, and copper in 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -0.800 V vs. sce into a mercury drop with a surface area of 0.032 cm² for 2 min with stirring plus 30 s without stirring	27
6	Anodic stripping voltammograms for total recoverable zinc, cadmium, lead, and copper in 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -1.200 V vs. sce into a mercury drop with surface area of 0.032 cm² for 2 min with stirring plus 30 s without stirring	28

Number | Page

7 Anodic stripping voltammograms for zinc, cadmium, lead, and copper in raw purified 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -1.200 V vs. sce into a mercury drop with a surface area of 0.032 cm^2 for 10 min with stirring plus 30 s without stirring 29

TABLES

Number		Page
1	Determinations of Hanging Mercury Drop Area	33
2	Simultaneous Determinations of Cadmium and Lead Concentrations by Anodic Stripping Voltammetry for Replicate Solutions of Spiked Reagent Water	34
3	Typical Sensitivities and Peak Height vs. Concentration Proportionality Tests for Cadmium, Lead, Copper, and Zinc	35
4	Effect of Ferric Iron and Hydroxylamine on Analysis of 30-µg/l Cadmium and Lead Samples by Anodic Stripping Voltammetry	36
5	Effect of Selenium (IV) and Ascorbic Acid on Analysis of 30-µg/l Cadmium and Lead by Anodic Stripping Voltammetry	37
6	Comparative Test Results of Cadmium and Lead Determinations for Split Samples from Ash Ponds	38
7	Test Results of Cadmium and Lead Determinations by Anodic Stripping Voltammetry for Standard Reference Samples	39
8	Simultaneous Determinations of Cadmium, Lead, and Copper by Anodic Stripping Voltammetry for Replicate Solutions of Spiked Reagent Water	39
9	Zinc Determinations by Anodic Stripping Voltammetry for Replicate Solutions of Spiked Reagent Water	40
10	Effect of Reaction Time on Purification of Ammonium Citrate Buffer by Electrolysis with Stirring into a Mercury Cathode at -1.500 V vs nce	40

Number | Page

11 Simultaneous Determination of Low Concentrations of Zinc, Cadmium, Lead, and Copper by Anodic Stripping Voltammetry with Purified Ammonium Citrate Buffer 41

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

A	--ampere
c-	--centi-, $X10^{-2}$ (as a prefix, e.g., cm)
°C	--degrees Celsius (centigrade)
EPA	--U.S. Environmental Protection Agency
g	--grams
HMDE	--hanging mercury drop electrode
hr	--hour
l	--liter
m	--meter
m-	--milli-, $X10^{-3}$ (as a prefix, e.g., mm)
min	--minute
M	--molar, mole per liter
n	--nano-, $X10^{-9}$ (as a prefix, e.g., ng)
N	--normal, equivalent per liter
NBS	--U.S. National Bureau of Standards
psi	--pound per square inch
ppm	--parts per million
PAR	--Princeton Applied Research
s	--second
t	--Student t statistic
TVA	--Tennessee Valley Authority
V	--volt
V vs. nce	--volts vs. a calomel electrode filled with 1 M potassium chloride
V vs. sce	--volts vs. a calomel electrode filled with saturated potassium chloride
w/v	--weight expressed as a fraction of total volume

SYMBOLS

μ-	--micro-, $X10^{-6}$ (as a prefix, e.g., μg)
%	--percent

SECTION 1

INTRODUCTION

Coal ash from steam-electric generating plants contains small amounts of cadmium, lead, copper, and zinc, which are deposited in ash sluicing water and settling ponds. Although these metals are largely removed by microflotation (1), some may eventually reach surface or ground waters.

As required by the Federal Water Pollution Control Act, test procedures have been published for determining concentrations of pollutants (cadmium, lead, copper, and zinc) by atomic absorption or colorimetry to demonstrate that effluent discharges meet applicable pollutant discharge limitations (2,3). Although not a compliance method, the determination of cadmium, lead, copper, and zinc at the level of micrograms per liter by anodic stripping voltammetry (ASV) has been a relatively common practice during the past few years (4-11).

Despite the recent use of ASV and the environmental, medical, and legal decisions made on the basis of results from ASV, a number of scientists seriously question the methods and the validity of determinations by ASV at the microgram level (4). The features and problems of trace metal analysis by ASV and atomic absorption spectroscopy, two of the most widely used methods for trace metal analysis, have been reviewed recently (4). Although concentrations of 22 metals may be determined by ASV (4), most applications are for zinc, cadmium, lead, and copper. ASV has been used to determine concentrations of zinc, cadmium, lead, and copper at nanogram and microgram levels in air samples (5), natural water (6-9), and sea water (8,10,11).

This study evaluates the validity of determinations of low concentrations of total recoverable cadmium, lead, copper, and zinc by ASV under carefully controlled conditions. The procedure is judged on the equivalence of its accuracy and reproducibility at low concentrations (0 to 100 µg/l) to the accuracy and reproducibility obtained by the standard reference methods at higher concentrations (greater than 50 µg/l) (2,3).

The principal objectives of this study are to establish favorable conditions for analyzing cadmium and lead by ASV and, afterwards, to modify the conditions for analysis of copper and zinc.

According to Meites (12,13), 0.25 M ammonium citrate buffer with a pH of 3 to 4 is an excellent electrolyte for analyzing zinc, cadmium, lead, and copper; 0.5 M or 0.025 M acetate at pH 6 is also suitable (6,7,12,13), especially when saturated with phenol (12). For this study 0.2 M ammonium citrate at pH 3.0 was chosen. A pH of 3.0 is sufficiently acidic to prevent hydrogen formation at -1.200 V vs. sce, thereby eliminating interference for the zinc stripping peak that appears at -1.200 V vs. sce. Also, because this pH falls within the optimum range determined by Sinko and Dolezal (7), small changes in pH will not affect the stripping peak heights for zinc, cadmium, lead, and copper.

Because digestion to dryness with nitric acid destroys organic matter that would otherwise cause interference patterns in the stripping voltammograms (14), wet ashing with nitric acid is chosen for sample preparation. Also, nitrate is weakly complexing and does not form the strong mercury complexes (such as Hg_2Cl_2) that would be formed if hydrochloric acid were used to digest samples. Such complexes cause interference by giving steeply sloping background currents close to the copper peak at about 0 V vs. sce (15).

According to Chau and Lum-Shue-Chan (6), iron (III) in 0.025 M acetate buffer at pH 6 interferes in the determination by ASV of zinc, cadmium, lead, and copper by depressing their peak currents. The authors overcome this interference by reducing the iron (III) to iron (II) with hydroxylamine. Iron (III) is an important interferer because its concentration in ash pond effluents from coal-fired power plants typically varies from 20 to 5100 µg/l (16). Another possible interferer is selenium (IV), which is present at concentrations often greater than 100 µg/l in ash pond effluents from coal-fired power plants (17); selenium (IV) is electrochemically active near the lead stripping peak (18-20). In this study both iron (III) and selenium (IV) were examined as possible interferers in the determination of zinc, cadmium, lead, and copper by ASV in 0.2 M ammonium citrate media at pH 3.2.

Surface area (and volume) of the electrode is a recognized variable that can influence formation of intermetallic amalgams, especially Zn(Cu). This amalgamation may lead to high stripping peaks for copper and low ones for zinc (21-23). Formation of amalgams is particularly serious when thin-film mercury electrodes are used because the small volume of mercury leads to a very high concentration of amalgams (21), especially at higher metal concentrations. Use of the hanging mercury drop minimizes this problem and increases the range of working concentration because of the larger volume of mercury (21). Because of this, a hanging mercury drop electrode (HMDE) with the largest possible surface area commensurate with a stable drop is used.

This report evaluates and describes a method of differential pulse ASV for determining total recoverable concentrations of cadmium and lead by (1) deposition in a mercury drop of known surface area at -0.800 V vs. sce and (2) anodic stripping to measure the peak currents. Section 4 of this report (1) describes the sample preparation, including digestion with nitric acid; (2) gives directions for eliminating interference from iron (III) by warming with hydroxylamine and eliminating interference from selenium (IV) by adding ascorbic acid; and (3) describes the optimum conditions for differential pulse ASV and the optimum surface areas for the HMDE that is used to measure cadmium and lead in 0.2 M ammonium citrate at pH 3.2. This technique is also applied, under similar conditions, to the determinations of (1) copper by deposition at -0.800 V vs. sce and (2) zinc by deposition at -1.200 V vs. sce. Reproducibility, detection limits, and sample blanks for analyses of concentrations ranging from 0 to 100 µg/l are critically evaluated.

SECTION 2

CONCLUSIONS

The Tennessee Valley Authority (TVA) used a method based on differential pulse ASV to determine total cadmium at concentrations of 0.3 to 100 µg/l and total lead at concentrations of 3 to 100 µg/l in aqueous ash pond effluents from coal-fired steam electric power plants. This method involves (1) evaporation to dryness with nitric acid; (2) warming with hydroxylamine in 0.2 M ammonium citrate (pH 3.0) to eliminate interference from 20,000 µg/l of iron (III); (3) addition of ascorbic acid to eliminate interference from 50 to 1000 µg/l of selenium (IV); (4) deposition at -0.800 V vs. sce into a mercury drop with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring; (5) measurement of the cadmium and lead currents by differential pulse ASV; and (6) determination by standard addition. Triplicate analyses at five concentrations show that cadmium and lead can be determined precisely. This method gives suitable accuracy for cadmium and lead in reference water samples and in split samples of effluent water from ash ponds that were analyzed by atomic absorption. Limited data show that this method probably is useful for 5 to 100 µg/l copper but, when modified for deposition at -1.200 V vs. sce, it is not useful for zinc because of a 15-µg/l sample blank for zinc.

SECTION 3

RECOMMENDATIONS

Differential pulse ASV is a suitable method for determining very low concentrations of total cadmium and lead in ash ponds that receive effluents from steam-electric generating plants.

Further studies should be conducted to determine the applicability of this method (1) to copper, (2) with digestion by ultraviolet irradiation instead of evaporation to dryness with nitric acid, and (3) to other process waste streams.

SECTION 4

EXPERIMENTAL

SAMPLE PREPARATION

Field Samples

Field samples were collected in January 1976 from ash ponds at all TVA coal-fired steam-electric generating plants and were analyzed for the presence of cadmium and lead. Those samples containing representative concentrations of these elements were selected for use in this study.

Standard Reference Samples

Standard reference samples for trace metals were obtained from the U.S. Environmental Protection Agency (EPA), and simulated precipitation reference materials for trace metals and minerals were obtained from the National Bureau of Standards (NBS). Both EPA and NBS reference samples, which consisted of known amounts of concentrated trace metals in very pure water, were diluted to the desired concentrations according to accompanying instructions.

Synthetic Samples

Test solutions containing 0, 5, 10, 30, 60, and 100 µg/l of cadmium and lead were prepared by spiking 10.0 ml of a solution of one volume of concentrated acid in 160 volumes of water [(1+160) nitric acid] with 5, 10, 30, 60, and 100 µl of a 10-ppm mixed standard of cadmium and lead in (1+160) nitric acid. Test solutions containing 30 µg/l cadmium, lead, and copper and 30 or 100 µg/l zinc, cadmium, lead, and copper were prepared similarly by spiking 10.0 ml of (1+160) nitric acid with appropriate amounts of 10-mg/l multielement standards. The 10,5,5,5- and 5,2.5,2.5,2.5-µg/l concentrations of zinc, cadmium, lead, and copper were prepared by spiking with 5 µl of the respective multielement concentrates of 20:10:10:10 and 10:5:5:5 mg/l. Some test solutions of 30 µg/l cadmium and lead were spiked with selenium (IV) to achieve concentrations of 30, 50, 100, 500, and 1000 µg/l. Other test solutions were prepared by spiking 5, 10, 20, and 40 mg/l iron (III) with cadmium and lead to achieve a concentration of 30 µg/l.

All elements used to prepare synthetic samples, except iron (III), were drawn from 1000-mg/l certified atomic absorption standards (Fisher Scientific Company, Fairlawn, New Jersey). The 1000-mg/l concentration of iron (III) was prepared gravimetrically from ferric ammonium sulfate dodecahydrate (8.634 g in 1000 ml of reagent water) with weights checked against reference weights certified at the NBS.

EQUIPMENT

All measurements were made with the Princeton Applied Research (PAR) Model 174 polarographic analyzer with HMDE and Houston omnigraphic X-Y recorder, Model 2200-3-3. The HMDE capillary was PAR Part No. 9303. Other instruments--the platinum counter electrode; the salt bridge with slow-leakage Vycor tip (Corning Glass Works, Corning, New York) to isolate the saturated calomel electrode from the test solution; the magnetic stirrer with uniform rotational speed; the outgassing tube; cell holder; and cell--were obtained from Princeton Applied Research Corporation (24). A 15- by 1.5-mm Teflon magnetic stirring bar (Bel-Art, Pequannock, New Jersey, Part No. F-37119) was used for ASV experiments with the PAR K62 polarographic cell bottom. An adjustable digital microliter pipet (Analtech, Newark, Delaware, Part No. P-20D or P-200D) was used to spike solutions.

PREPARATION OF EQUIPMENT AND SOLUTIONS

The HMDE was cleaned and siliconized by standard procedures to prevent thread withdrawal and noisy voltammograms (25). It was also necessary to rinse the HMDE by aspiration with nitric and chromic acid, followed by thorough rinsing with reagent water (26), and to bake it at 110°C just before siliconizing and use; this procedure also minimized thread withdrawal.

The surface area of the hanging mercury drop dispensed by the HMDE was determined gravimetrically. Figure 1 gives a plot of the surface area of a drop vs. the micrometer reading for dispensing that drop for a manually operated HMDE (PAR Part No. 9323). A mercury drop with a surface area of 0.032 cm^2, corresponding to six small micrometer divisions, was used in the voltammetric determinations given in this report. Raw micrometer readings (Table 1) plus surface areas calculated by equation (1) in the following discussion are plotted in Figure 1.

Surface area values were obtained by extruding, for each micrometer setting in small vertical divisions, a series of ten drops from the HMDE while it was located beneath 4 ml of water in a 5-ml beaker. After the water was poured off and the residue was rinsed with three 3-ml portions of acetone, the weight of the beaker plus mercury was determined; after the mercury was discarded the beaker was reweighed. The difference divided by

ten gave the weight of a single mercury drop. This weight was used to calculate surface area for a mercury drop formed by extrusion:

$$\text{Surface area of mercury drop, cm}^2 = 4\pi\left(\frac{3W}{4\pi\rho}\right)^{2/3} , \qquad (1)$$

where W = weight of a single mercury drop, g,
ρ = density of mercury for the temperature at which the determination was made, g/cm^3 (27).

Calculations were made by entering W and ρ into a calculator programmed to yield surface areas directly (28).

Voltammetric cells were cleaned by soaking them overnight in concentrated nitric acid. Other glassware that contacted the sample solution was soaked overnight in a solution of two volumes of concentrated nitric acid in three volumes of water. After leaching, the glassware was rinsed with reagent water and dried in an oven at 110°C. Clean glassware and digested sample solutions were covered with Parafilm (Fisher Scientific Company, Fairlawn, New Jersey) to prevent contamination from trace elements in atmospheric particles.

Nitrogen gas, used to deaerate solutions for polarographic analysis, was purged of oxygen. Zero-grade nitrogen gas was passed through a furnace containing a special catalytic converter (a gas purifier, Model 02-2315, purchased from Supelco, Bellefonte, Pennsylvania) and heated to 600°C. After the gaseous effluent from the furnace was passed successively through a Hydro-Purge unit and a Dow Gas Purifier (Applied Science Laboratories, State College, Pennsylvania), it was passed through sintered glass frits in three scrubbing towers. One scrubbing tower contained 100 ml of reagent water, and the other two contained 100 ml of 0.1 M chromous chloride in 2.4 M hydrochloric acid with amalgamated zinc. The amalgamated zinc particles used in the Jones reductor (Fisher Scientific Company, Fairlawn, New Jersey) were 0.8 to 3.2 mm in diameter. Details for preparing the chromous chloride scrubbers are given by Meites (12).

Reagent-grade chemicals were used to prepare all solutions except (1) the redistilled nitric acid that was used to digest the samples, (2) the 1 M potassium chloride used in the reference electrode of the electrolysis purification cell, and (3) the 0.2 M ammonium citrate buffer, which was purified further in an electrolysis cell for some determinations of low metal

concentrations. The redistilled nitric acid was purchased from G. Frederick Smith Company, 867 McKinley Avenue, Columbus, Ohio 43223. The 1 M potassium chloride was prepared from an "Ultrex" grade salt (Baker Chemical Company, Phillipsburg, New Jersey) by dissolving 7.45 g of the salt in reagent water and diluting the solution to 100 ml. The 0.2 M ammonium citrate buffer was prepared by dissolving 42 g citric acid in about 800 ml reagent water, adding enough ammonium hydroxide to bring the pH to 3.0±0.2, and diluting the solution to 1000 ml. The buffer was sterilized by autoclaving for 15 min at 121°C and 1.03×10^5 Pascals (15 pounds per square inch). Because this sterilization eliminated bacterial growth for only a month, the buffer was newly prepared each month.

For experiments with low metal concentrations, the 0.2 M ammonium citrate buffer was purified further in a reagent purifier system (PAR Model 9500) by electrolysis at -1.500 V vs. nce into a mercury pool working electrode. The supporting electrolyte was deaerated and stirred during purification. The calomel reference electrode was filled with 1 M potassium chloride, which was prepared from the "Ultrex" grade salt, to minimize metal contamination from the salt solution in the reference electrode. The counter electrode was a coiled, 22-guage platinum wire (Fisher Scientific Company, Fairlawn, New Jersey) in a salt bridge with unpurified ammonium citrate that contacted the solution through a Vycor disk. A black precipitate slowly formed on the disk between the platinum counter electrode and the citrate buffer. This was eliminated by electrolyzing the buffer at -1.300 V vs. nce, which effectively removed zinc, cadmium, lead, and copper from the buffer.

The 10 percent hydroxylamine solution (100 g/l as the hydrochloric acid salt) was free of iron and copper (G. Frederick Smith Chemical Company, 867 McKinley Avenue, Columbus, Ohio 43223). The 10 percent (w/v) ascorbic acid reagent was prepared by dissolving 10 g of L-ascorbic acid powder in reagent water and diluting to 100 ml. The (1+160) nitric acid was prepared by diluting 1 volume of nitric acid with 160 volumes of reagent water, and the (2+3) nitric acid was prepared by diluting 2 volumes of nitric acid with 3 volumes of water.

DETERMINATION OF CADMIUM AND LEAD BY ASV

The samples were digested by adding 2.0 ml of redistilled nitric acid to 10.0 ml of sample in a 50-ml beaker and evaporating the solution on a hot plate without boiling until the sample just reached dryness. Baking beyond dryness was avoided to prevent possible losses by volatilization. After the sample was cooled, 5.0 ml of 0.2 M ammonium citrate buffer (pH 3.0) and 100 µl of 10 percent (w/v) hydroxylamine (except when noted otherwise) were added. The solution was warmed 15 min to reduce

iron (III) and to dissolve the metals in the buffer. The solution was transferred quantitatively to the voltammetric cell and brought to a volume of 10 to 12 ml with the ammonium citrate buffer. The cell was precalibrated at about 11 ml by etching it with a diamond-tipped pencil. The exact volume need not be known when standard additions are used to quantitate. In some of the experiments (as noted) to eliminate interference by selenium (IV), 1 ml of 10 percent (w/v) ascorbic acid was added to the solution in the cell.

A stirring bar was inserted into the solution, and the solution was deaerated for 10 min at 100 ml/min with nitrogen gas that had been treated to remove oxygen. A mercury drop, with a surface area of 0.032 cm^2, was extruded by rotating the HMDE micrometer six small vertical divisions (see Figure 1). The magnetic stirrer was turned on, and the stirring rate was adjusted so that the solution beneath the mercury drop was well stirred without visible movement of the mercury drop. The stirrer was turned on 15 s before deposition to assure uniform rotational speed.

After connecting the voltammetric cell, cadmium and lead were determined by deposition in the mercury drop at -0.800 V vs. sce for exactly 2 min with stirring and then allowing convection currents to cease for 30 s without stirring. Immediately thereafter, a differential pulse anodic voltammetric scan was made between -0.800 and -0.200 V vs. sce under suitable conditions. The peak for cadmium appeared at about -0.600 V vs. sce, and the one for lead appeared at about -0.420 V vs. sce. Typical conditions used for the PAR 174 polarographic analyzer were initial potential, -0.800 V vs. sce; scan rate, 5 mV/sec; range, 0.750 V; scan direction, positive; modulation amplitude, 25 mV; sensitivity, 2 μA for 0 to 10 μg/l of cadmium and lead, 5 μA for 20 to 50 μg/l of cadmium and lead, and 10 μA for 60 to 100 μg/l of cadmium and lead; drop time, 0.5 s; display direction, negative; operation mode, differential pulse; output offset, negative settings as required. With the Houston omnigraphic 2200-3-3 recorder, recorder Y-axis was adjusted to 1 V/in. (0.039 V/mm) and X-axis was adjusted to 100 mV/in. (3.94 mV/mm).

To calculate unknown concentrations of cadmium and lead in samples, the method of standard addition was used (12). After the differential pulse anodic stripping curve for the sample was determined, an appropriate aliquot of cadmium and lead stock solution (usually 10 mg/l) was added to the sample (normally between 5 and 100 μl) in the cell by use of an adjustable digital microliter pipet, and the solution was deaerated for an additional 5 min to mix the solution and remove oxygen added with the spike. Thereafter, another differential pulse anodic stripping curve was determined under conditions identical to

those for determining the sample. The concentration of each metal was calculated by the equation given by Meites (12):

$$C_2 = \frac{i_1 v C_1 (1000)}{i_2 v + (i_2 - i_1)(V)(1000)}, \qquad (2)$$

where i_1 = stripping peak height for the sample, μA,
i_2 = stripping peak height for the sample plus standard, μA,
v = volume of standard taken for spiking, μl,
V = volume of sample dispensed for digestion, ml,
C_1 = concentration of standard used to spike, mg/l,
C_2 = concentration of the unknown in the sample, μg/l.

Calculations were made by entering i_1, v, C_1, i_2, and V into a calculator programmed to yield C_2 directly in micrograms per liter (28).

DETERMINATION OF COPPER AND ZINC BY ASV

Concentrations of copper alone or cadmium, lead, and copper were determined under the same conditions as were concentrations of cadmium and lead except that the differential-pulse anodic voltammetric scan was made between -0.80 and +0.10 V vs. sce, and the range was 1.500 V. The peak for copper appeared at about -0.030 V vs. sce.

Concentrations of zinc alone or zinc, cadmium, lead, and copper were determined under nearly the same conditions as were concentrations of cadmium and lead except that the deposition was conducted at -1.200 V vs. sce, the voltammetric scan was made between -1.200 and +0.100 V vs. sce, and the range was 1.500 V. The peak for zinc appeared at about -1.000 V vs. sce.

Low concentrations of zinc, cadmium, lead, and copper were determined simultaneously under the same conditions as were concentrations of zinc except that a 10-min deposition was used.

SECTION 5

RESULTS AND DISCUSSION

A sensitive method of differential pulse ASV was developed for determining cadmium and lead in aqueous ash pond effluents from coal-fired steam-electric power plants. This method involves evaporating a 10.0-ml sample to dryness with 2.0 ml of concentrated, redistilled nitric acid; warming with 100 µl of 10 percent (w/v) hydroxylamine in 0.2 M ammonium citrate (pH 3.0) to eliminate interference from 20,000 µg/l of iron (III); adding 1 ml of 10 percent (w/v) ascorbic acid to eliminate interference from 50 to 1000 µg/l of selenium (IV); depositing at -0.800 V vs. sce into a mercury drop with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring; measuring the cadmium and lead current by differential pulse ASV; and determining cadmium and lead concentrations by standard addition. As a result of this and other work, a version of this method of ASV has been published as a proposed standard in Part 31 of the 1977 Annual Book of Standards, American Society of Testing and Materials (29). The method described in Section 4 is being interlaboratory tested (29). In addition, limited data indicate that this method is probably useful for determining concentrations of copper but, when modified for deposition at -1.200 V vs. sce, it is probably not useful for determining zinc because of the high sample blanks.

Inspection of data in Table 2 for simultaneous determination of cadmium and lead by ASV for replicate solutions of spiked reagent water reveals that (1) the range of the method is 0.3 to 100 µg/l for cadmium and 3 to 100 µg/l for lead and (2) the lowest quantifiable concentration of the method is limited by the sample blank, which is about 0.3 µg/l total recoverable cadmium and 3 µg/l lead. The precision and accuracy with which cadmium and lead are recovered by this method from triplicate standard solutions containing 5, 10, 30, 60, and 100 µg/l of both metals were determined by standard additions (12). Table 2 gives the analytical results. Respectively, the standard deviations are 0.6, 2.4, 4.6, 2.0, and 9.1 µg/l for cadmium and 1.2, 2.1, 3.0, 0.0, and 8.0 µg/l for lead; the relative standard deviations are 11.1, 22.8, 15.9, 3.8, and 9.9 percent for cadmium and 19.0, 18.4, 10.0, 0.0, and 8.4 percent for lead; and the percentage accuracies (biases) are +8.0, +5.0, -3.3, -11.7, and -8.0 for cadmium and +26, +14, 0.0, -6.7, and -5.0 for lead (30). According to a one-sample t test, the percentage accuracies, except those at 60 µg/l, are not statistically significant at the

95 percent confidence level (31). This information aids in establishing the validity of trace analyses by this method at 0 to 100 µg/l (4).

Figure 2 gives typical differential pulse anodic stripping voltammograms for total recoverable concentrations of cadmium and lead in 0.2 M ammonium citrate buffer (pH 3.0) by deposition at -0.800 V vs. sce in a mercury drop with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring. As shown in Figure 2, the stripping voltammograms are well defined for both cadmium and lead at 10 and 100 µg/l. This verifies that the conditions proven for analysis at high concentrations by polarography (voltammetry at the dropping mercury electrode) (12,13) are equally applicable to analysis at low concentrations by differential pulse ASV at the HMDE. Table 3 gives typical sensitivities (in microamperes per microgram per liter) of cadmium and lead in digested samples and in samples spiked for quantitation by standard additions. These data illustrate (1) linearity of the method up to at least 100 µg/l of cadmium and lead and (2) the extreme sensitivity of both elements--about 0.03 $\mu A\ \mu g^{-1}\ l^{-1}$ for cadmium and 0.02 $\mu A\ \mu^{-1}\ l^{-1}$ for lead.

One disadvantage is that, even when sterilized, the ammonium citrate (pH 3.0) electrolyte in which cadmium and lead are determined will not resist bactericlogical growth indefinitely; it gives erratic voltammograms about a month after sterilization and therefore must be prepared each month. For this reason alone, the 0.025 M sodium acetate (pH 6) used by Chau and Sinko (6,7) may be equally suitable, although Meites (12) claims that the results for cadmium are improved when the acetate is saturated with phenol.

It is well known that 0.0007 percent (w/v) hydroxylamine hydrochloride eliminates the suppression of anodic stripping peaks of cadmium and lead that is caused by 280 µg/l iron (III) in 0.04 M sodium acetate (pH 6) (6). The interference from 20,000 µg/l of iron (III) on the anodic stripping peaks for 30 µg/l of cadmium and lead in 0.2 M ammonium citrate (pH 3.0) is eliminated by warming the solution for 15 min with hydroxylamine hydrochloride in 5.0 ml of 0.2 M ammonium citrate buffer (pH 3.0) in a concentration of 0.1 percent (w/v) (100 µl of 10 percent hydroxylamine for 10 ml of sample analyzed). Many ash pond effluents from coal-fired steam-electric power plants contain iron (III), but most of them contain iron (III) in maximum concentrations of 5,100 µg/l (16). Dilution may be required for samples that contain more than 20,000 µg/l iron (III), such as drainage from strip mines.

Table 3 displays raw data for 30 µg/l of cadmium and lead recovered from 10.0 ml of aqueous standards containing 5000, 10,000, 20,000, or 40,000 µg/l of iron (III) that were (1)

digested with nitric acid, (2) treated with 0, 100, or 500 µl of 10 percent (w/v) hydroxylamine, and (3) analyzed by differential pulse ASV in 0.2 M ammonium citrate (pH 3.0). As shown in Table 4, the addition of 100 µl of 10 percent (w/v) hydroxylamine gives nearly quantitative recoveries of 30 µg/l of cadmium and lead in the presence of 5000, 10,000 and 20,000 µg/l of iron (III). The absence of hydroxylamine causes high results at 20,000 µg/l iron (III). At 40,000 µg/l iron (III), an erratic baseline is observed at voltages more positive than -0.350 V vs. sce. This behavior warns that the level of iron (III) is higher than the analytical method can tolerate.

Selenium (IV), which was determined in some ash pond effluents in concentrations of 100 µg/l (17), may interfere because it has a stripping peak at voltages near those voltages at which lead has a stripping peak (18-20). Figure 3 shows that, at -0.340 V vs. sce, 30 µg/l of selenium (IV) appears as a slight shoulder on the stripping peak caused by 30 µg/l of lead. The selenium (IV) shoulder is more evident at 50 µg/l. At 100 µg/l the selenium (IV) peak is well defined and causes a depression in the lead peak from about 0.6 to 0.2 µA (see Figure 3) that leads to the low results for lead in Table 5. Figure 4 illustrates that 1000 µg/l of selenium (IV) causes a depression in not only the lead but also the cadmium peaks at 30 µg/l that makes their determination impossible. However, as seen in Figure 4, the addition of 1 ml of 10 percent (w/v) ascorbic acid before the sample is deaerated destroys the selenium (IV) peak and restores the cadmium and lead peaks to their normal values. The data in Table 5 prove that ascorbic acid can be added to give a satisfactory analysis of cadmium and lead at 30 µg/l in the presence of 100, 500, and 1000 µg/l of selenium (IV). Ascorbic acid is not necessary at selenium (IV) concentrations below 50 µg/l; the appearance of the selenium (IV) shoulder adjacent to the stripping peak for lead indicates that ascorbic acid is needed.

The method of differential pulse ASV described in Section 4 was compared with the reference atomic absorption method (3) for recovering cadmium and lead from samples of effluent water taken from ash ponds in the Tennessee Valley. The reference atomic absorption method was used to recover cadmium and lead that are soluble in hot, dilute HCl-HNO_3 with chelation by ammonium pyrrolidine dithiocarbonate and concentration by solvent extraction with methylisobutylketone to improve sensitivity (3). Analytical results are given in Table 6 for concentrations of cadmium and lead recovered from the split samples of ash pond water by the ASV and atomic absorption methods. Although severely limited, the data on split samples in Table 6 indicate that the two methods compare favorably. Most of these samples contained too little cadmium and lead to give a measurable amount by atomic absorption, which, even with concentration by solvent

extraction, cannot determine the concentrations that can be quantitated by the ASV method described in this report.

Concentrations of cadmium and lead have been determined in standard reference water samples (32,33). Our test results, which are given in Table 7, agree reasonably well with the certified values.

The ASV method for recovering cadmium and lead by digestion with nitric acid and deposition at -0.800 V vs. sce in ammonium citrate buffer was also tested for determining copper concentrations by scanning to a voltage of +0.100 V vs. sce rather than ending the scan at -0.200 V vs. sce. Table 8 shows that copper, as well as cadmium and lead, is recovered in quantifiable concentrations by standard addition from triplicate standard solutions of 30 μg/l cadmium, lead, and copper and 30 μg/l zinc, cadmium, lead, and copper. The lowest quantifiable concentration of copper is limited to the sample blank, which is about 5 μg/l. The stripping voltammograms in Figure 5 for 30 μg/l of cadmium, lead, and copper give well-defined peaks for total recoverable copper quantified by standard addition with a sensitivity of about 0.04 $\mu A\ \mu g^{-1}\ l^{-1}$. Exact sensitivities for copper are listed in Table 3.

By changing the deposition voltage to -1.200 V vs. sce, this method was tested for zinc recovered by standard addition from triplicate standard solutions of 100 μg/l zinc and 100 μg/l zinc, cadmium, lead, and copper. Table 9 shows that fairly quantitative recoveries of zinc are possible, but that erratic recoveries are probably caused by a high sample blank of 15 μg/l. Figure 6 gives the voltammograms for the four metals analyzed simultaneously by digestion, ASV analysis in citrate media, and quantitation by standard additions. The sensitivity of the method for zinc is about 0.02 $\mu A\ \mu g^{-1}\ l^{-1}$, which is about the same as that for cadmium (see Table 3).

A high concentration of copper causes amalgamation of copper and zinc when a sufficiently high concentration of zinc is present during the deposition in a mercury drop or film of sufficiently small volume (21). The copper-zinc amalgam is stripped with the copper peak; this causes high stripping currents for copper and low stripping currents for zinc (21-23). As shown in Table 9, the presence of 100 μg/l of copper does not affect the recovery of 100 μg/l of zinc, probably because of the low concentrations tested, the large volume of the HMDE, and the short deposition period. The absence of interference by copper on zinc in our study agrees with the work of Shuman and Woodward in which an HMDE with a volume of 6.23×10^{-4} cm^3 was used (21). In our study the volume of the HMDE is 5.38×10^{-4} cm^3, which corresponds to a surface area of 0.032 cm^2. The interference by copper on zinc is more severe with electrodes plated with a thin

film of mercury because their volume is 1.44×10^{-7} cm^3 (21), which is about 3700 times smaller than the HMDE used in our study.

In an attempt to lower sample blanks for zinc, cadmium, lead, and copper, the electrolytically purified 0.2 M ammonium citrate (pH 3.0) was tested for determination of low concentrations of the four metals simultaneously. After 192 hr of purification, assay of the raw 0.2 M ammonium citrate buffer (pH 3.0) by differential pulse ASV after deposition at -1.200 V vs. sce for 10 min leads to values of 1.0, <0.2, 0.5, and 0.2 for zinc, cadmium, lead, and copper, respectively (Table 10). Voltammograms are shown in Figure 7. But after the reagent water is digested and the metal concentrations are quantified in the purified ammonium citrate, the zinc, cadmium, lead, and copper values increase to 7 to 9, 0.2 to 0.3, 1.4 to 2.1, and 0.3 to 2.7 µg/l, respectively (Table 11). As shown in Tables 2, 8, and 9, the respective sample blanks are 14 to 15, 0.1 to 0.3, 0.8 to 3.4, and 2.4 to 5.3 µg/l for digesting reagent water and quantifying concentrations in unpurified citrate. Purification does not improve the sample blanks for cadmium and lead, but it does improve the blanks for copper and zinc by a factor of two. Thus, comparison of the values before and after digestion, with and without purification, shows that digestion is the principal source of contamination in the lead blank, but that it accounts for only half of the contamination in the zinc and copper blanks. The cadmium blank is not a problem, probably because it is not found ubiquitously.

Table 11 gives results for zinc, cadmium, lead, and copper at concentrations of 10,5,5,5 and 5,2.5,2.5,2.5 µg/l analyzed by ASV. To minimize blanks, Blutstein and Bond (34) suggest that analysis of very low concentrations be performed without digestion directly on samples acidified with nitric acid; however, some industrial effluents give interference patterns in the anodic stripping voltammograms that must be eliminated by digestion with nitric acid (14). The sample blanks for lead, copper, and zinc probably can be improved by digestion by ultraviolet irradiation in quartz tubes with hydrogen peroxide and hydrochloric acid added (8,35).

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violet Irradiation in the Determination of Nutrients in Water with Special Reference to Nitrogen. Technical Bulletin No. 40, Inland Waters Branch, Department of Energy, Mines and Resources, Ottawa, Canada, 1971. p. 22.

FIGURES

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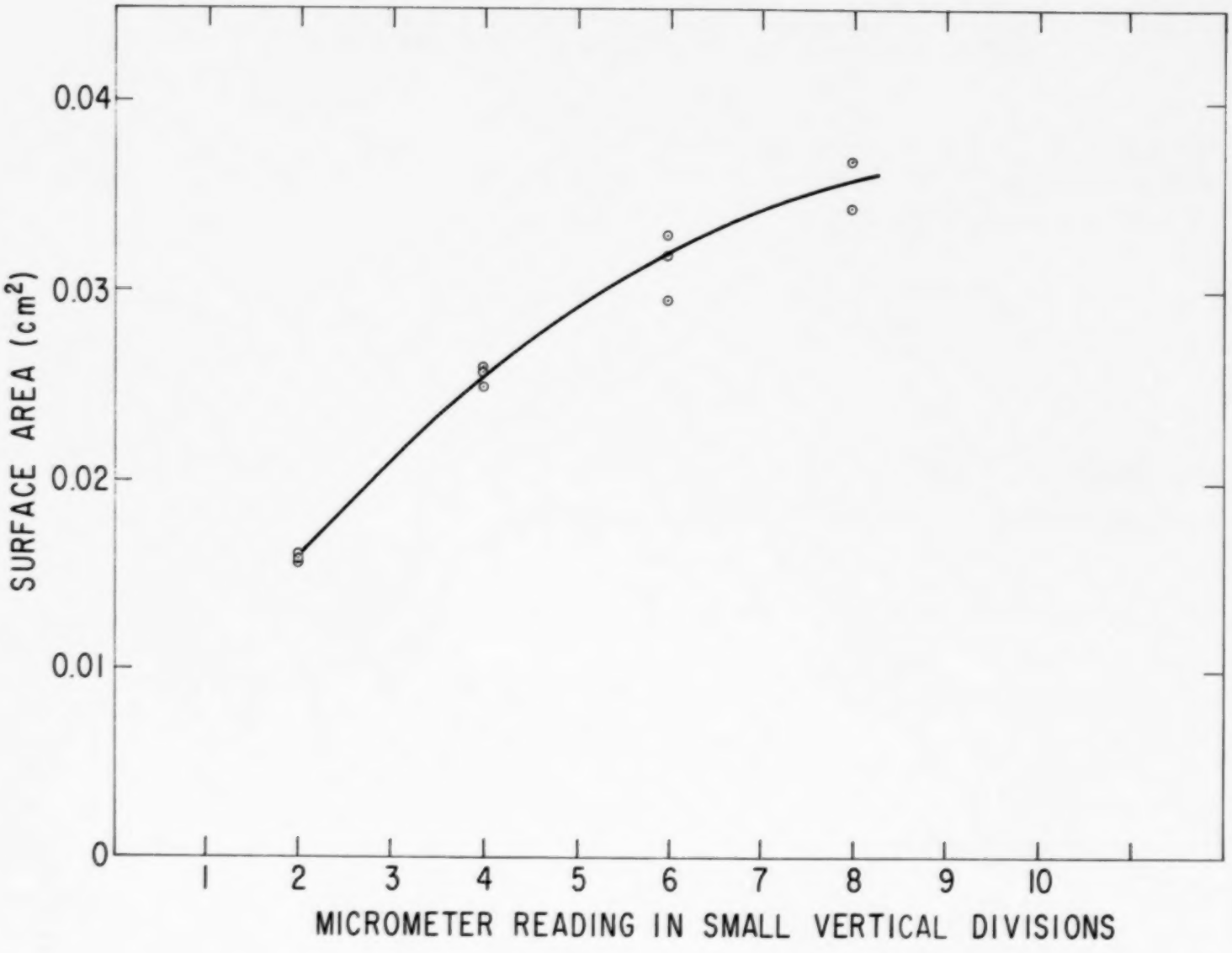

Figure 1. Calibration curve for surface area of mercury drop formed by extrusion with a manually operated hanging mercury drop electrode.

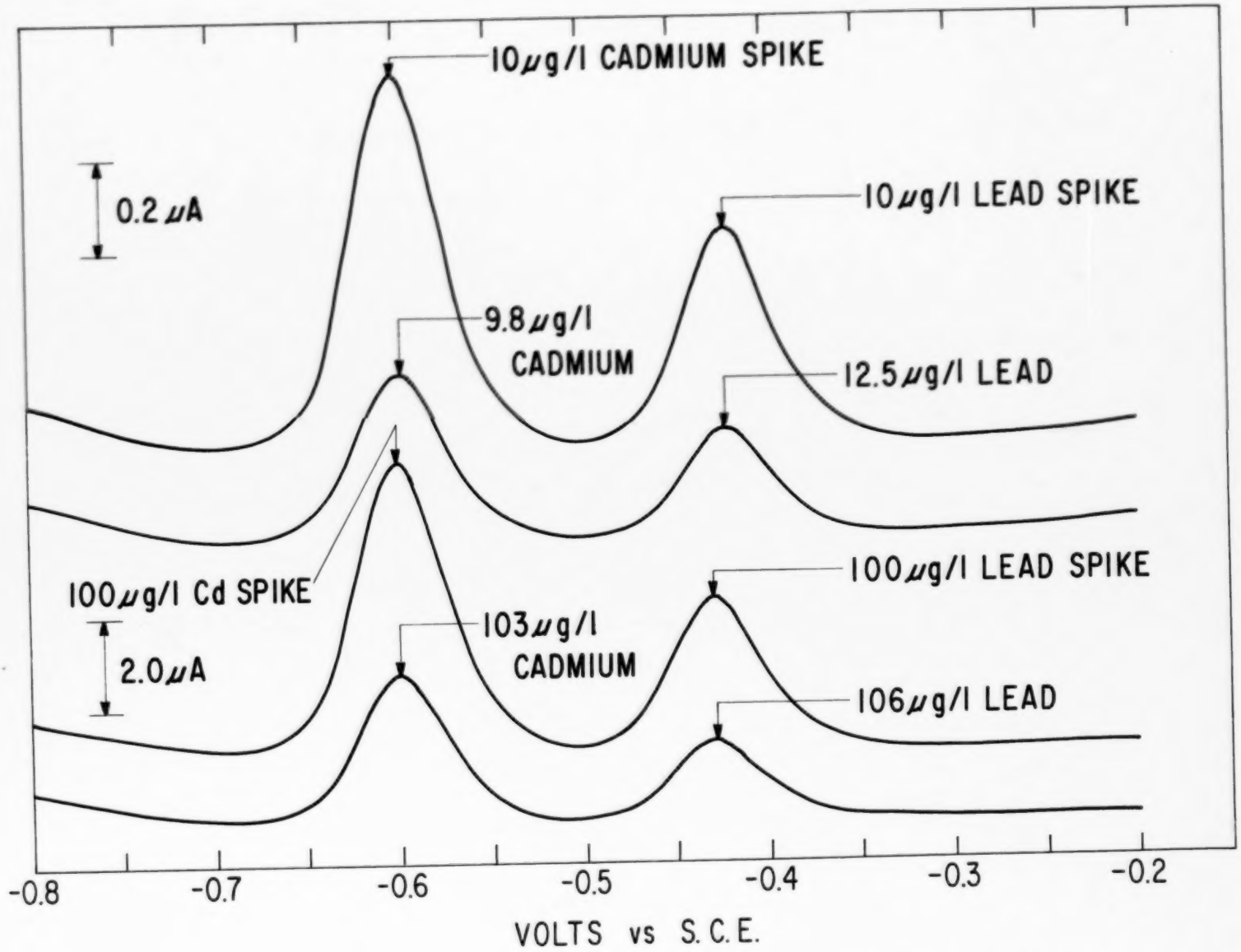

Figure 2. Anodic stripping voltammograms for total recoverable cadmium and lead in 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -0.800 V vs. sce into a mercury droplet with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring.

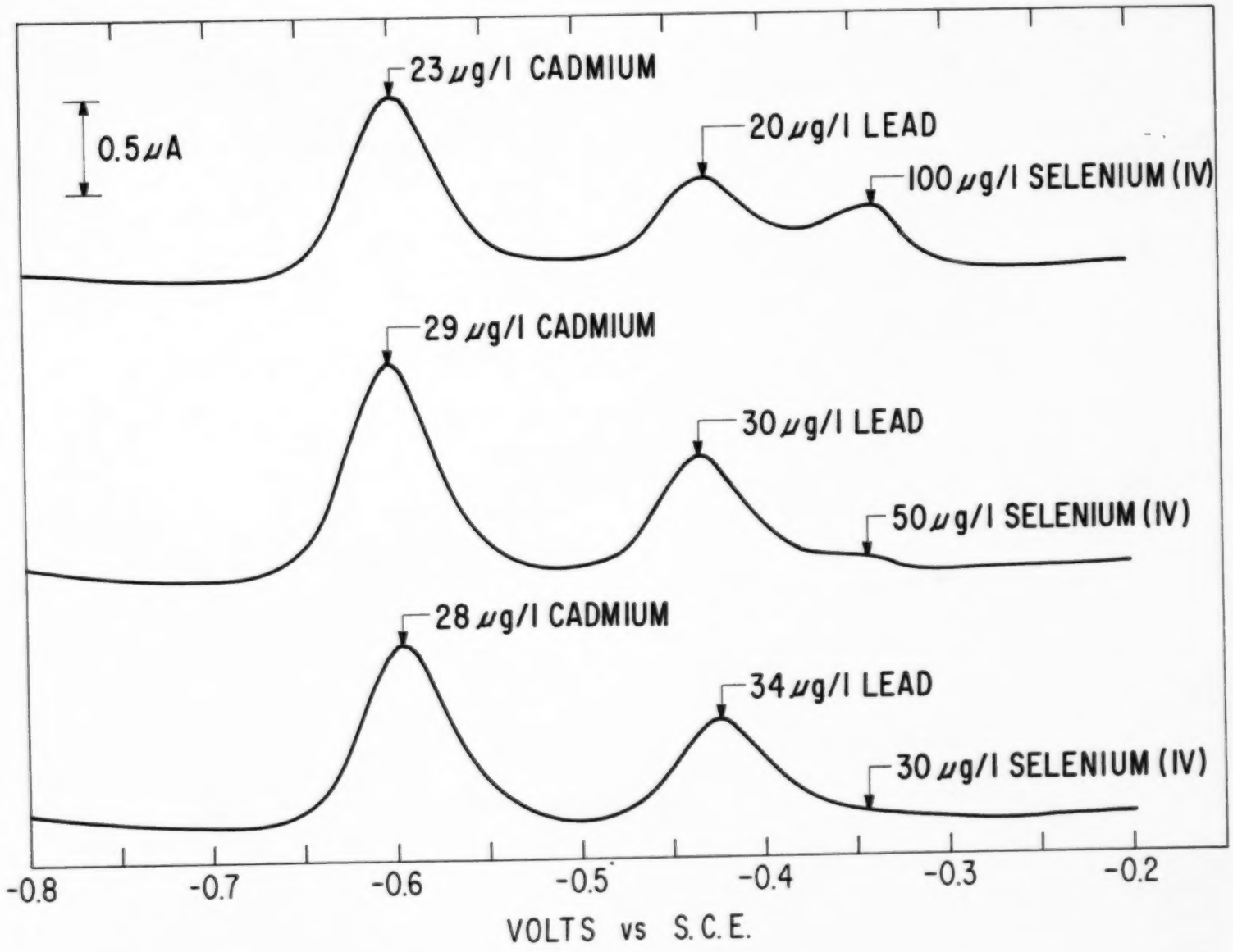

Figure 3. Interference of selenium (IV) on anodic stripping voltammograms for total recoverable cadmium and lead in 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -0.800 V vs. sce into a mercury drop with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring.

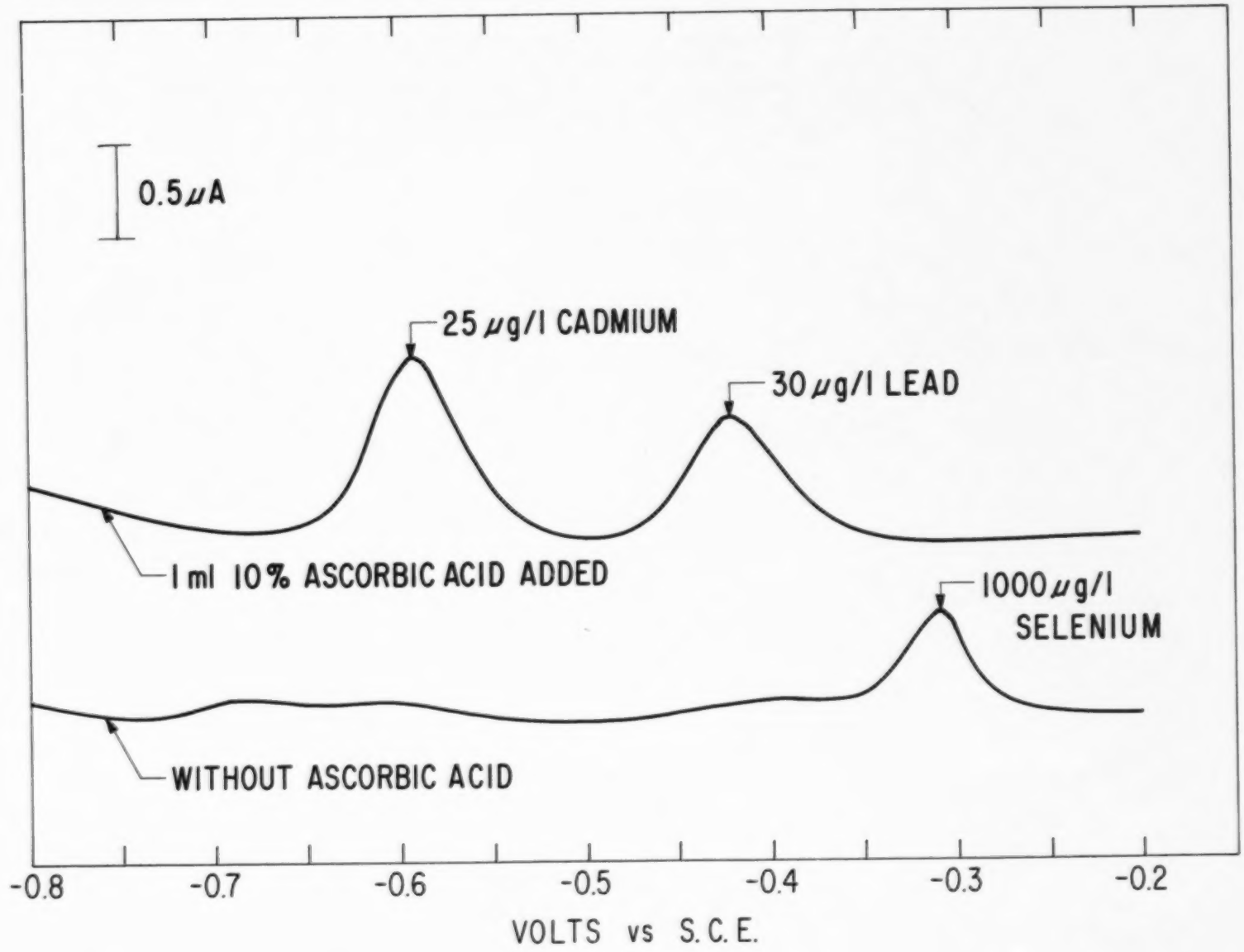

Figure 4. Ascorbic acid for eliminating interference of selenium (IV) on anodic stripping voltammograms for total recoverable cadmium and lead in 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -0.800 V vs. sce into a mercury droplet with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring.

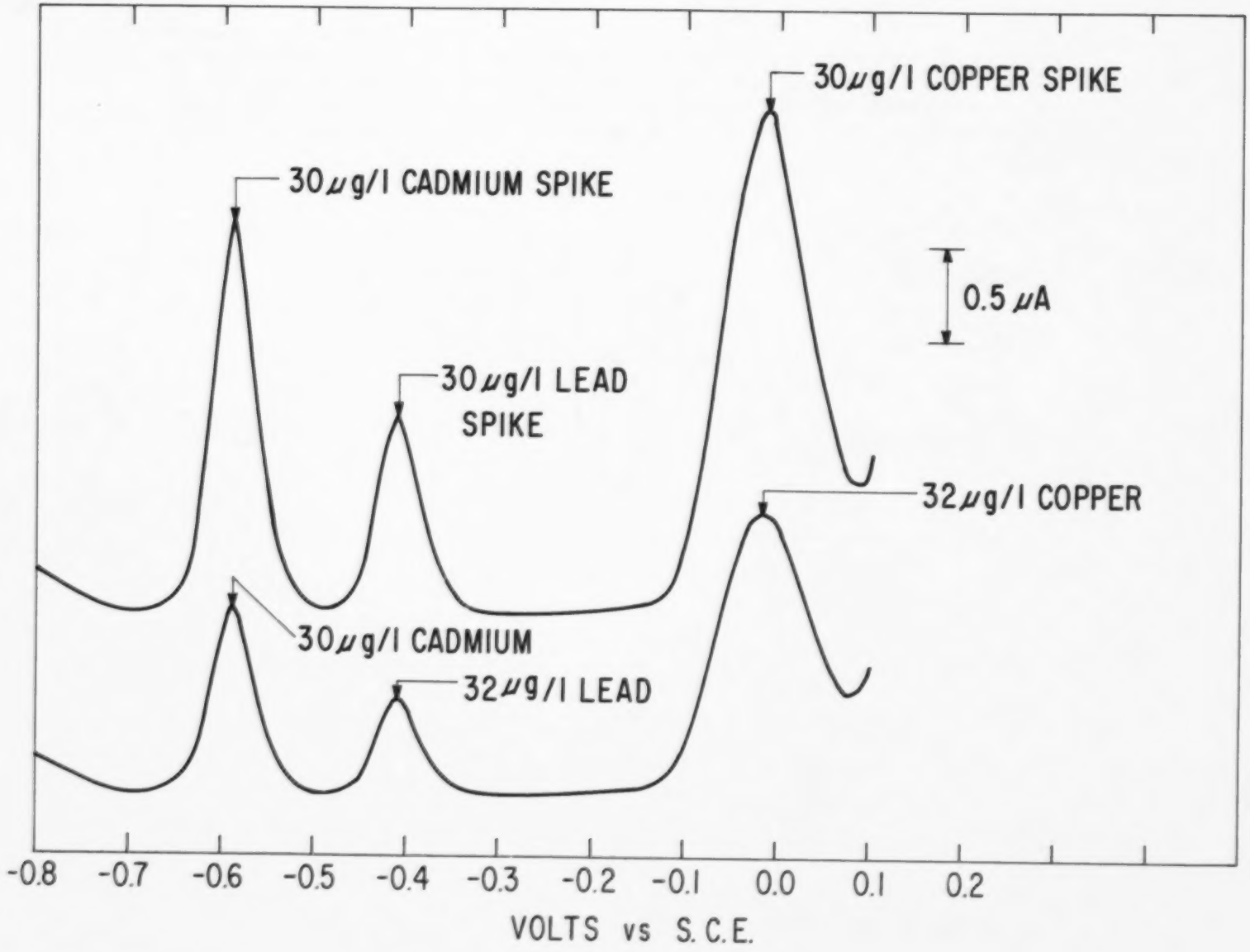

Figure 5. Anodic stripping voltammograms for total recoverable cadmium, lead, and copper in 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -0.800 V vs. sce into a mercury drop with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring.

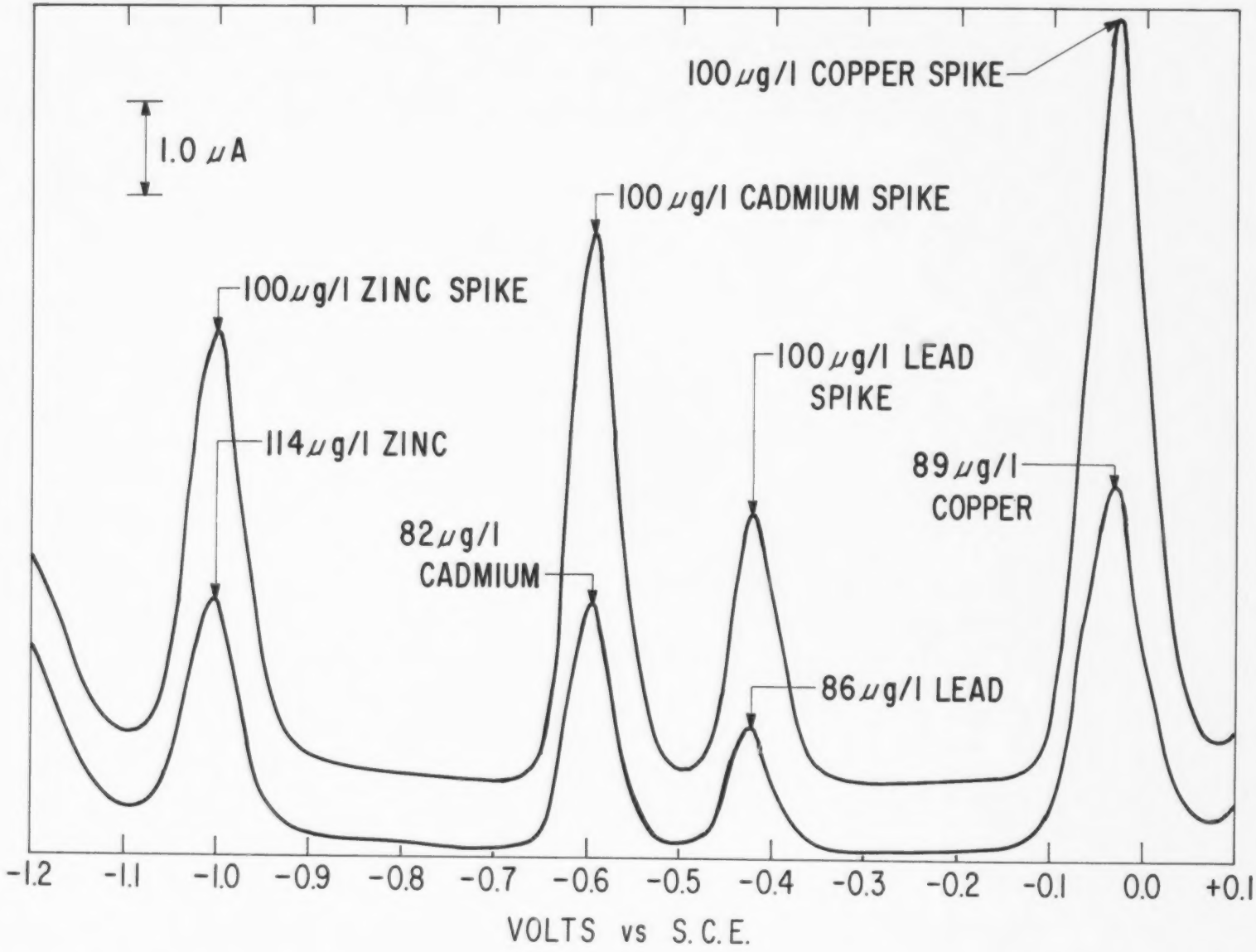
100 µg/l COPPER SPIKE
1.0 µA
100 µg/l CADMIUM SPIKE
100 µg/l ZINC SPIKE
100 µg/l LEAD SPIKE
114 µg/l ZINC
89 µg/l COPPER
82 µg/l CADMIUM
86 µg/l LEAD
-1.2 -1.1 -1.0 -0.9 -0.8 -0.7 -0.6 -0.5 -0.4 -0.3 -0.2 -0.1 0.0 +0.1
VOLTS vs S.C.E.

Figure 6. Anodic stripping voltammograms for total recoverable zinc, cadmium, lead, and copper in 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -1.200 V vs. sce into a mercury drop with surface area of 0.032 cm² for 2 min with stirring plus 30 s without stirring.

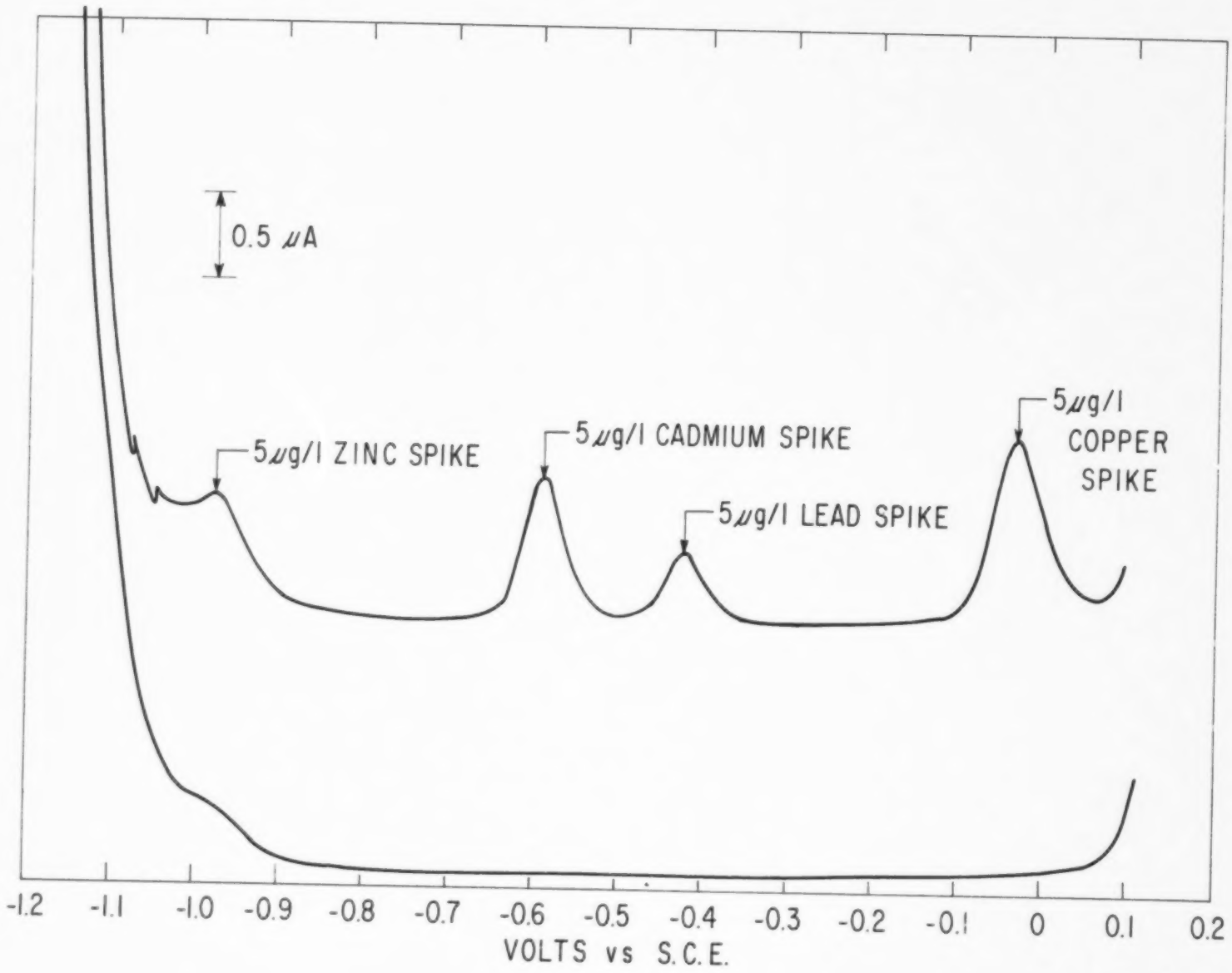
0.5 μA
5μg/l ZINC SPIKE
5μg/l CADMIUM SPIKE
5μg/l LEAD SPIKE
5μg/l COPPER SPIKE
-1.2 -1.1 -1.0 -0.9 -0.8 -0.7 -0.6 -0.5 -0.4 -0.3 -0.2 -0.1 0 0.1 0.2
VOLTS vs S.C.E.

Figure 7. Anodic stripping voltammograms for zinc, cadmium, lead, and copper in raw purified 0.2 M ammonium citrate buffer at pH 3.0 by deposition at -1.200 V vs. sce into a mercury drop with a surface area of 0.032 cm^2 for 10 min with stirring plus 30 s without stirring.

TABLES

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TABLE 1. DETERMINATIONS OF HANGING MERCURY DROP AREA

Reading (small vertical divisions)	Temperature (°C)	Weight of 10 drops (mg)	Surface area per drop (cm^2)
2	22.8	24.97	0.01567
2	22.8	25.43	0.01586
2	22.8	25.53	0.01590
4	22.8	50.05	0.02491
4	22.8	53.20	0.02594
4	22.8	52.87	0.02584
6	23.1	64.59	0.02953
6	23.1	64.89	0.02962
6	22.8	72.80	0.03198
6	22.8	76.17	0.03296
8	22.8	81.52	0.03448
8	22.8	90.54	0.03698

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TABLE 2. SIMULTANEOUS DETERMINATIONS OF CADMIUM AND LEAD CONCENTRATIONS BY ANODIC STRIPPING VOLTAMMETRY FOR REPLICATE SOLUTIONS OF SPIKED REAGENT WATER[a]

Cadmium and lead concentration (µg/l)	Cadmium determination (µg/l)	Lead determination (µg/l)
0	0.2, 0.1, 0.1, 0.1, 0.2, 0.1, 0.2, 0.2, 0.3, 0.2, 0.2, 0.1, 0.2	1.9, 2.5, 2.8, 0.8, 1.8, 3.0, 3.4, 2.6, 3.4, 2.4, 3.2, 2.9, 3.0
5.0	6.0, 4.8, 5.5	6.5, 7.4, 5.1
10.0	8.7, 9.6, 13.3	10.2, 10.3, 13.8
30	25, 34, 28	27, 33, 30
60	53, 55, 51	56, 56, 56
100	102, 91, 84	103, 94, 87

[a] Determination was made by deposition at -0.800 V vs. sce in a mercury drop with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring.

TABLE 3. TYPICAL SENSITIVITIES AND PEAK HEIGHT VS. CONCENTRATION PROPORTIONALITY TESTS FOR CADMIUM, LEAD, COPPER, AND ZINC[a]

Metal	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
	Raw 1[b]	10-µg/l Spike[c]	Raw 2[b]	30-µg/l Spike[c]	Raw 3[b]	60-µg/l Spike[c]	Raw 4[b]	100-µg/l Spike[c]	Raw 5[b]	30-µg/l Spike[c]	Raw 6[b]	100-µg/l Spike[c]
Cadmium												
µA	0.388	0.784	0.995	1.87	1.90	4.02	3.09	6.04				
µg/l	9.78	19.78	33.9	63.9	53.2	113.2	102.6	202.6				
µA µg^{-1} l^{-1}	0.0397	0.0396	0.0293	0.0293	0.0357	0.0355	0.0301	0.0298				
Lead												
µA	0.254	0.456	0.510	0.950	1.08	2.16	1.64	3.15				
µg/l	12.54	22.54	34.5	64.5	59.3	119.3	106.3	206.3				
µA µg^{-1} l^{-1}	0.0203	0.0202	0.0148	0.0147	0.0182	0.0181	0.0154	0.0152				
Copper												
µA									1.20	2.33		
µg/l									31.6	61.6		
µA µg^{-1} l^{-1}									0.0380	0.0378		
Zinc												
µA											2.41	4.48
µg/l											113.7	213.7
µA µg^{-1} l^{-1}											0.0212	0.0210

[a] Determinations of cadmium, lead, and copper were made by deposition at −0.800 V vs. sce in a mercury drop with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring. Determinations of zinc were made by deposition at −1.200 V vs. sce under the same conditions.

[b] Raw 1, 2, 3, and 4 are digested standard mixtures 10, 30, 60, and 100 µg/l of cadmium and lead. Raw 5 and 6 are digested standards with 30 µg/l copper and 100 µg/l zinc.

[c] Spike is the standard addition used to quantitate the raw sample adjacent to it.

TABLE 4. EFFECT OF FERRIC IRON AND HYDROXYLAMINE ON ANALYSIS OF 30-µg/l CADMIUM AND LEAD SAMPLES BY ANODIC STRIPPING VOLTAMMETRY[a]

Ferric iron concentration (µg/l)	Cadmium determination (µg/l)	Lead determination (µg/l)
	No hydroxylamine	
20,000	36	50
40,000[b]	24	33
	100 µl of 10% hydroxylamine	
5,000	32	34
10,000	30	30
20,000	33, 24, 24, 20	66, 32, 34, 24
40,000[b]	24	34
	500 µl of 10% hydroxylamine	
20,000	24	24
40,000[b]	27	26

[a]Determination was made by deposition at -0.800 V vs. sce in a mercury drop with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring.

[b]At 40,000 µg/l Fe(III), an erratic baseline is observed at voltages more positive than -0.350 V vs. sce, the region where the tail end of the stripping peak for lead appears.

TABLE 5. EFFECT OF SELENIUM (IV) AND ASCORBIC ACID ON ANALYSIS OF 30-µg/l CADMIUM AND LEAD SAMPLES BY ANODIC STRIPPING VOLTAMMETRY[a]

Selenium concentration (µg/l)	Cadmium determination (µg/l)	Lead determination (µg/l)
	No ascorbic acid	
30	27	32
50	28	27
100	23	17
	1 ml of 10% ascorbic acid	
100	31	29
500	29	36
1000	25	27

[a]Determination was made by deposition at -0.800 V vs. sce in a mercury drop with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring.

TABLE 6. COMPARATIVE TEST RESULTS OF CADMIUM AND LEAD DETERMINATIONS FOR SPLIT SAMPLES FROM ASH PONDS

Location	Cadmium (µg/l)		Lead (µg/l)	
	Voltammetric[a]	Atomic absorption	Voltammetric[a]	Atomic absorption
Allen	9.7	10, 12	16	<10, <10
Bull Run	0.6	<1, <1	10, 12	<10, <10
Colbert	<0.2	<1, <1	7.2	<10, <10
Cumberland	<0.2	<1, <1	4.0	<10, <10
Gallatin	0.4	<1, <1	7.3	<10, 11
John Sevier[b]	5.8	5.2, 7.0	7.2	<10, <10
John Sevier[c]	<0.2	<1, <1	15	<10, <10
Johnsonville	0.2	<1, 2	8.0	<10, <10
Kingston	2.8	1.1	15	<10, <10
Paradise[b]	128, 106	120, <1	34, 36	34
Paradise[c]	1.5	<1, <1	6.0	<10, <10
Shawnee	0.3	<1, 3	4.0	<10, <10
Watts Bar	2.4	<1, 3	8.0	<10, <10
Widows Creek	0.2	<1, <1	4.6	<10, <10

[a] Determination was made by deposition at -0.800 V vs. sce in a mercury drop with a surface area of 0.032 cm^2 for 2 min with stirring plus 30 s without stirring.

[b] Samples of water from the fly ash pond were collected and analyzed.

[c] Samples of water from the bottom ash pond were collected and analyzed.

TABLE 7. TEST RESULTS OF CADMIUM AND LEAD DETERMINATIONS BY ANODIC STRIPPING VOLTAMMETRY FOR STANDARD REFERENCE SAMPLES[a]

Description	Cadmium (µg/l)		Lead (µg/l)	
	Certified	Voltammetric	Certified	Voltammetric
EPA trace metals reference sample 575 (No. 1)	5.2	5.5	22	27
	Recommended	Voltammetric	Recommended	Voltammetric
NBS simulated precipitation reference sample A	30	34	18	16
NBS simulated precipitation reference sample C	578	510	152	170

[a]Deposition was made at -0.800 V vs. sce in a mercury drop with surface area of 0.032 cm² for 2 min with stirring plus 30 s without stirring.

TABLE 8. SIMULTANEOUS DETERMINATIONS OF CADMIUM, LEAD, AND COPPER BY ANODIC STRIPPING VOLTAMMETRY FOR REPLICATE SOLUTIONS OF SPIKED REAGENT WATER[a]

Concentration of cadmium, lead, and copper (µg/l)	Cadmium determination (µg/l)	Lead determination (µg/l)	Copper determination (µg/l)
	No zinc		
0	0.2	1.9	5.3
30	27, 29, 30	30, 34	25, 29, 26
	With 30 µg/l zinc		
0	0.2	1.6	2.4
30	25, 23, 29	25, 24, 28	27, 26, 30

[a]Determination was made by deposition at -0.800 V vs. sce in a mercury drop with a surface area of 0.032 cm² for 2 min with stirring plus 30 s without stirring.

TABLE 9. ZINC DETERMINATIONS BY ANODIC STRIPPING VOLTAMMETRY FOR REPLICATE SOLUTIONS OF SPIKED REAGENT WATER[a]

Zinc concentration (µg/l)	Zinc determination (µg/l)
0	14
100	69, 99, 79
	With 100 µg/l cadmium, lead, and copper
0	15
100	93, 99

[a]Determination was made by deposition at -1.200 V vs. sce in a mercury drop with a surface area of 0.032 cm² for 2 min with stirring plus 30 s without stirring.

TABLE 10. EFFECT OF REACTION TIME ON PURIFICATION OF AMMONIUM CITRATE BUFFER BY ELECTROLYSIS WITH STIRRING INTO A MERCURY CATHODE AT -1.500 V vs. nce[a]

	Metal determination (µg/l)			
Reaction time (hr)	Zinc	Cadmium	Lead	Copper
Raw solution	11	0.2	2.5	3.3
19	4.1	<0.2	1.6	0.6
48	2.7	<0.2	0.5	0.3
168	1.0	0.2	0.7	0.3
192	1.0	<0.2	0.5	0.2

[a]Determination was made by deposition at -1.200 V vs. sce in a mercury drop with a surface area of 0.032 cm² for 2 min with stirring plus 30 s without stirring.

TABLE 11. SIMULTANEOUS DETERMINATION OF LOW CONCENTRATIONS OF ZINC, CADMIUM, LEAD, AND COPPER BY ANODIC STRIPPING VOLTAMMETRY WITH PURIFIED AMMONIUM CITRATE BUFFER [a]

Metal	Solution 1 (µg/l)			Solution 2 (µg/l)		
	Concentration	Determination[b]	Blank	Concentration	Determination[b]	Blank
Zinc	10	9±7	9	5	2±3	7
Cadmium	5	5.0±1.8	0.3	2.5	2.7±0.8	0.2
Lead	5	4.2±1.6	2.1	2.5	2.5±1.1	1.4
Copper	5	3.8±2.1	2.7	2.5	4.4±1.7 [c]	0.3

[a]Determination was made by deposition at -1.200 V vs. sce in a mercury drop with a surface area of 0.032 cm^2 for 10 min with stirring plus 30 s without stirring. The ammonium citrate buffer that was used in the determination was purified to values of 1.0, <0.2, 0.5, and 0.2 µg/l for zinc, cadmium, lead, and copper, respectively, by electrolysis into a mercury cathode at -1.500 V vs. nce.

[b]Average value and standard deviation for triplicate determinations minus blank determination.

[c]From a duplicate determination.